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SHORT COMMUNICATION

TEM observation of nonamphiphilic copolymer micelles

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Abstract Light scattering and transmission electron microscope (TEM) measurements were preformed for micelles of a nonamphiphilic poly(vinylphenol)-*block*-polystyrene diblock copolymer (*PVPh*-*b*-PSt) to determine the shape of the micelles. The micelles were prepared by the self-assembly of the copolymer in 1,4-dioxane, a nonselective solvent, in the presence of 1,4-butanediamine. The logarithm of the normalized time correlation function of the scattered field, $\ln G_1(\tau)$, linearly decayed versus the delay time, τ. The diffusion coefficient measured in the range of the scattering angles from 30° to 150° was almost independent of the square of the magnitude of the scattering vector. The linear decay of $\ln G_1(\tau)$ vs τ and the angular-independence of the diffusion coefficient suggested that the monodisperse spherical micelles were formed by the micellization. The TEM observations confirmed the formation of uniform spheres.

Keywords Poly(vinylphenol)-*block*-polystyrene · A nonamphiphilic block copolymer · 1,4-Butanediamine · Monodisperse spherical micelles · Light scattering · TEM observation

Introduction

Micelles are nanoscale supramolecules formed not only naturally, but also artificially, by molecular self-assembly through noncovalent bonding such as van der Waals interaction, electrostatic attraction, and hydrogen bonding. The micelles can solubilize and stabilize substances by taking them into the micellar cores. The micelles have many applications as dispersing agents and stabilizers in industry. Examples include carriers in drug delivery [1, 2], stabilizers in food processing [3, 4], dispersing agents for coal–water mixture fuels [5] and for coatings of dyeing and painting [6], and surfactants in water purification [7] and in extraction technologies [8]. Recently, many publications have been released on the micelle formation of block copolymers. The micelle formation concerns not only the direct micellization of amphiphilic copolymers [9–11], but also the indirect micellization of nonamphiphilic copolymers consisting entirely of solvophilic blocks. The indirect micellization is induced by variation in the external parameters such as temperature [12, 13], pressure [14–16], pH [17, 18], and salt formation [19, 20]. During the micellization, molecularly dissolved nonamphiphilic copolymers are converted in situ to amphiphilic copolymers by these stimuli. Hence, the indirect micellization has many advantages over the direct micellization. There is no dependence on the solubility balance of the solvophilic and solvophobic moieties when designing the nonamphiphilic copolymers. It is able to provide a better selection of the driving force. In addition, a variety of amphiphilic copolymers can be created from one nonamphiphilic copolymer in situ by selecting the stimuli.

I have recently observed the micelle formation of nonamphiphilic copolymers using the interaction with additives [21–27]. The poly(vinylphenol)-*block*-polystyrene diblock copolymer (PVPh-*b*-PSt) is self-assembled into micelles in nonselective solvents in the presence of α, ω-diamine [28–32]. The micelles were formed by the hydrogen bond cross-linking between the PVPh blocks via the diamine. Due to the unusual micelle formation, the shape of the micelles has been attracting increasing

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attention. I revealed that the PVPh-*b*-PSt copolymer formed spherical micelles with the diamine based on a light scattering study and transmission electron microscopy (TEM) observations. This article describes the light scattering studies and TEM observations of the micelles.

Experimental

Instrumentation Light scattering measurements were performed by a Photal Otsuka Electronics ELS-8000 electrophoretic light scattering spectrophotometer equipped with a system controller, an ELS controller, and a He–Ne laser operating at λ=632.8 nm and also by a Photal Otsuka Electronics DLS-7000 super dynamic light scattering spectrometer equipped with LS-71 control unit, an LS-72 pump controller, and an argon ion laser operating at λ= 488 nm. TEM measurements were performed with a JEOL JEM-2010 electron microscope.

Materials PVPh-*b*-PSt was prepared as reported previously [31]. The molecular weight of the copolymer was Mn (PVPh-*b*-PSt) = 10,000-*b*-120,000 by ^{1}H NMR. 1,4-Butanediamine (BDA) was distilled over calcium hydride. 1,4-Dioxane was purified by refluxing on sodium for several hours and distilled over sodium.

Light scattering measurements PVPh-*b*-PSt (10 mg) was dissolved in 1,4-dioxane (3 ml) and, using a syringe, the resulting solution was injected through a microporous filter into a cell. The solution was subjected to light scattering measurements at 10 °C. After the measurement, 24 μl of BDA solution [BDA (148 mg, 1.68 mmol) in 1 ml of 1,4-dioxane] was added to the copolymer solution in the cell, and the mixture was vigorously shaken. The solution was allowed to stand at 10 °C for 5 min and then subjected to light scattering again.

TEM observation A drop of the micellar solution was allowed to fall on a Cu grid with a carbon substrate, and the solvent was immediately evacuated using a filter paper. The grid was dried in air for a few hours and then subjected to TEM measurements.

Results and discussion

The time correlation function of the scattered intensity is given by Eq. 1

$$G_2(\tau) = A\left(1 + \beta|G_1(\tau)|^2\right) \quad (1)$$

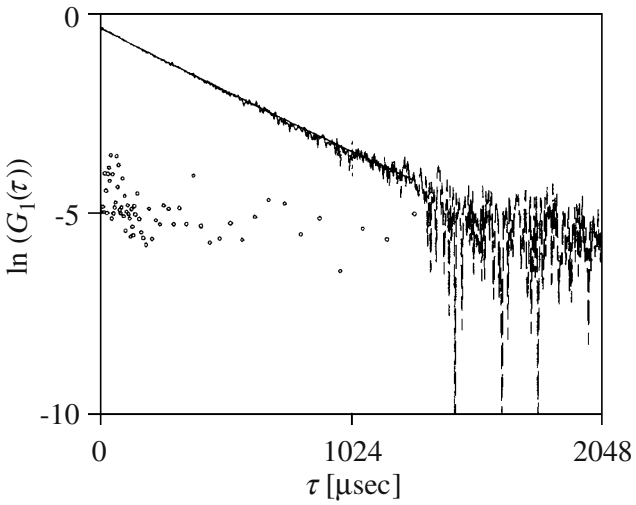

Fig. 1 The plots of $\ln G_1(\tau)$ vs τ for the PVPh-*b*-PSt micelles prepared at BDA/VPh of 6 at 10 °C in 1,4-dioxane at a copolymer concentration of 3.33 mg/ml. The scattering angle θ=90°

where A is a baseline that corresponds to the square of the average scattering intensity, β is an efficiency factor, and $G_1(\tau)$ is the normalized time correlation function of the scattered field. For spherical particles with a monodispersity, $G_1(\tau)$ displays a single exponential decay curve and is represented by Eqs. 2 and 3

$$G_1(\tau) = \exp(-\Gamma\tau) \quad (2)$$

$$\ln(G_1(\tau)) = -\Gamma\tau \quad (3)$$

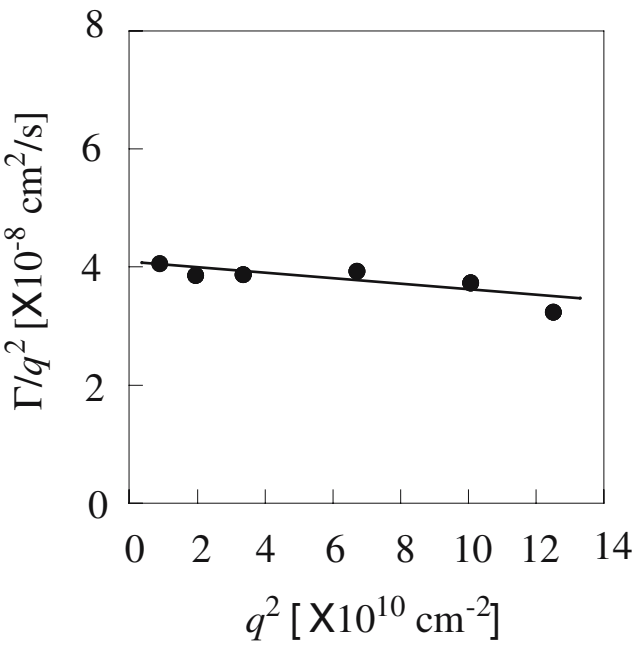

Fig. 2 The plots of D vs q^2 for the PVPh-*b*-PSt micelles prepared at BDA/VPh of 3 at 10 °C in 1,4-dioxane at a copolymer concentration of 3.33 mg/ml

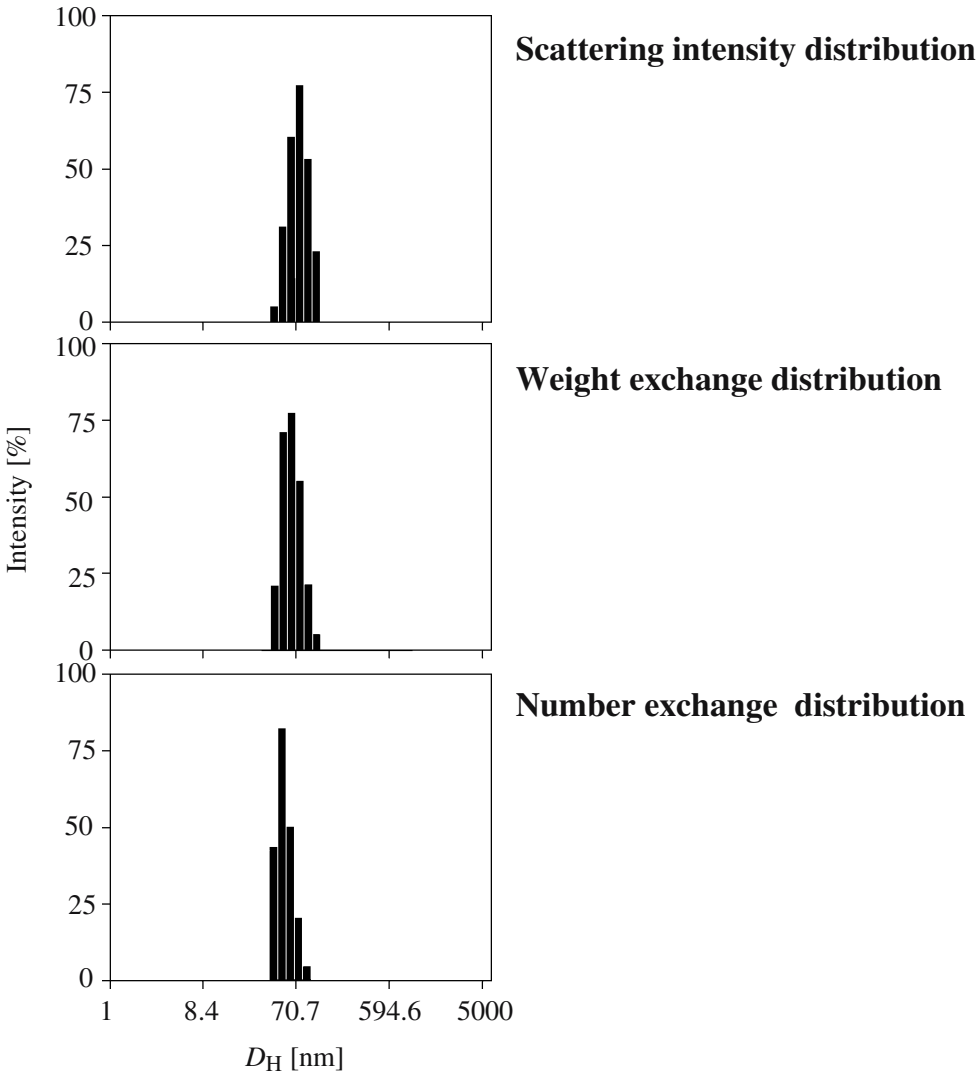

Fig. 3 The diameter distributions obtained by the Marquadt analysis of the PVPh-*b*-PSt micelles prepared at BDA/VPh of 6 in 1,4-dioxane at 10 °C at a copolymer concentration of 3.33 mg/ml. θ=90°

where Γ is a decay constant and τ is a delay time [33]. The PVPh-*b*-PSt diblock copolymer produced micelles at 10 °C in 1,4-dioxane in the presence of BDA over a molar ratio of 3 for the BDA the VPh unit (BDA/VPh) [31]. The hydrodynamic diameter of the micelles was unchanged over a BDA/VPh of 3; however, the micelles prepared at a BDA/VPh of 6 were more thermally stable than those at 3. Figure 1 shows the plots of the $\ln G_1(\tau)$ versus τ for the micelles prepared at the BDA/VPh of 6. The $\ln G_1(\tau)$ linearly decayed vs τ, suggesting the formation of nearly monodispersed spherical micelles.

The analysis of the angular dependence of the micelles also supported the formation of nanospheres with a narrow size distribution. The decay constant Γ is represented as Eqs. 4 and 5

$$\Gamma = q^2 D \tag{4}$$

$$q = (4\pi n_0/\lambda_0)\ \sin(\theta/2) \tag{5}$$

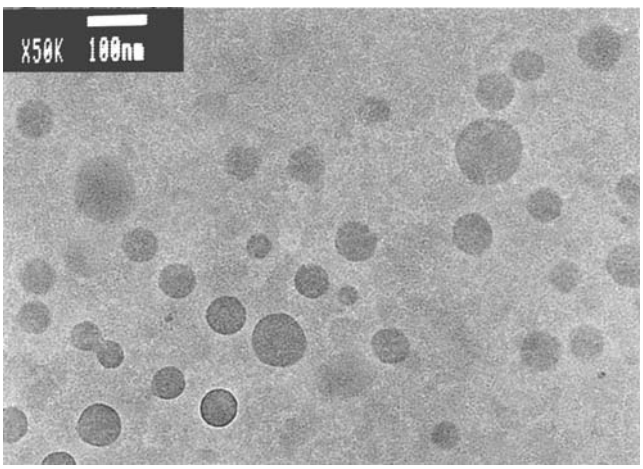

Fig. 4 The TEM image of the PVPh-*b*-PSt micelles prepared at BDA/VPh of 6 at 10 °C in 1,4-dioxane at a copolymer concentration of 3.33 mg/ml

where q is the magnitude of the scattering vector, D is the diffusion coefficient, n_0 is the solvent refractive index, λ_0 is the wavelength of the laser, and θ is the scattering angle. The diffusion coefficient, $D = \Gamma/q^2$ measured in the scattering angle range from 30° to 150° was almost independent of q^2 for the micelles (Fig. 2). This angular-independence of the diffusion coefficient was also observed for the micelles prepared in other nonselective solvents such as THF and ethyl acetate, although the amount of BDA required for the micellization varied with the solvent. It is suggested that PVPh-*b*-PSt produces spherical micelles with a narrow size distribution in these solvents in the presence of BDA.

The hydrodynamic diameter of the micelles prepared at the BDA/VPh of 6 in 1,4-dioxane was estimated to be 64.3 nm by the cumulant analysis, whereas the aggregation number was 15 based on the relative scattering intensity [15, 29]. Figure 3 shows the following three different distributions obtained by the Marquadt analysis [34] of the micelles: scattering intensity distribution, weight exchange distribution, and number exchange distribution. The hydrodynamic diameters of the micelles were estimated to be D_H(Is) = 70.5±16.5 nm by the scattering intensity distribution, D_H(wt) = 59.8±14.1 nm by the weight exchange distribution, and D_H(no) = 51.8±10.5 nm by the number exchange distribution. The distribution index of the hydrodynamic diameter was D_H(wt)/D_H(no) = 1.15 based on the weight exchange and number exchange distributions.

The TEM observations revealed that spherical micelles were formed by the self-assembly of PVPh-*b*-PSt by BDA. The TEM image of the micelles is shown in Fig. 4. Almost complete spheres were observed for the PVPh-*b*-PSt micelles. The weight average diameter of the micelles was estimated to be D(wt) = 78.5 nm, whereas the number average diameter was as D(no) = 65.0 nm based on the TEM measurements. The distribution index of the diameter is given by the following equation [35]

$$D_{(\mathrm{wt})}/D_{(\mathrm{no})} = \left\{\Sigma \mathrm{N}_i D_i^4 / \left(\Sigma \mathrm{N}_i D_i^3\right)\right\} / \left\{\Sigma \mathrm{N}_i D_i / \Sigma \mathrm{N}_i\right\} \qquad (6)$$

where N_i is the number of particles with diameter D_i. The size distribution was estimated to be D(wt)/D(no) = 1.21. There is a small difference in the size distributions estimated by the TEM and light scattering methods. The number average diameter was in good agreement with that determined by the cumulant analysis, indicating that the micelles in the solution maintained their size in air. In some cases, amphiphilic copolymer micelles showed a smaller size in the TEM than that in light scattering due to swelling of the micellar cores in solution. The cores of the PVPh-*b*-PSt micelles consist of the PVPh blocks cross-linked by BDA. Therefore, the micellar size should be independent of the presence of the solvent molecules in the cores.

Conclusions

The light scattering and TEM measurements confirmed that the PVPh-*b*-PSt and BDA produced spherical micelles with a narrow size distribution. The micellar size estimated by the cumulant analysis during the light scattering was in good agreement with that by the TEM observations. This negligible difference in size implied that the micelles in the solution maintained their size in air on the basis of the cross-linked cores of the PVPh blocks by BDA. There was also a small difference in the size distribution between the light scattering and TEM observations. This is the first study demonstrating that the nonamphiphilic block copolymer formed spherical micelles by the interaction with the additive. This micelle formation is expected to be a new method for preparing nanospheres with a narrow size distribution.

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